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Thermal stability of polymers confined in graphite oxide

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Abstract

In this study, polymer-graphite oxide (GO) interactions are demonstrated to induce thermal instability in both the polymer and GO phase in conditions of maximum polymer uptake, in which the polymer chains are either intercalated into the GO interlayer or adsorbed on the GO sheets. We investigate the thermal stability of poly(ethylene oxide) (PEO) intercalated in GO (PEO/GO) in detail, using a combination of techniques including X-ray diffraction (XRD), thermogravimetry (TGA) and TGA-Mass Spectroscopy (TGA-MS) in dynamic (nonisothermal) and static (isothermal) modes. Our results show that intercalated PEO decomposes at 160 °C lower than neat PEO, and that GO decomposes at 50 °C lower than pristine GO, due to a synergistic instability between GO and intercalated PEO upon heating. Other hydrophilic polymers—such as poly(vinyl methyl ether) (PVME), poly(vinyl alcohol) (PAA), poly(vinyl pyrrolidone) (PVP) and poly(acrylic acid) (PAA)—forming polymer-adsorbed GO structures are also observed to decompose at noticeably lower temperatures than either pristine GO or their own corresponding neat polymers. Unlike PEO/GO intercalation compounds, the excess of PEO phase in PEO-GO composites decomposes at temperatures close to that of neat PEO, which demonstrates that those polymer chains far from the adsorbing GO surface are not significantly affected by the presence of GO sheets. Furthermore, isothermal TGA data for PEO/GO intercalation compounds with PEO chains from 5 to 2135 monomeric units are well described by an autocatalytic model similar to that we found for pristine GO in a previous study, which suggests that the overall decomposition of PEO/GO is dominated by the reduction and exfoliation of GO. However, when PEO is adsorbed on graphene substrate, which is thermally stable at the studied temperatures, the kinetic mechanisms follow a first-order reaction similar to neat PEO, but the decomposition occurs with a considerably lower activation energy.

Introduction

High thermal stability of polymer-based composites is a fundamental prerequisite for manufacturing high quality devices. This prerequisite is usually (but not always) fulfilled by combining

the higher thermal stability of nanofillers with achieving good dispersibility in a polymer matrix. In this context, the chemical nature of the functional groups at the surface of the filler is extremely important in assessing polymer-filler interactions. GO, a low cost precursor of graphene, has been used as a filler in reinforced polymer composites.[1] Its thermal stability is lower than that of graphene, due to the presence of oxygen-functional groups at the GO surface such as epoxide, hydroxyl, ketone, carboxylic acid, lactone, etc.[2,3] These groups decompose at relatively low temperatures (ca. 150 °C for GO obtained by Hummers' method and ca. 250 °C for that obtained by Brodie's method) by a disproportionation reaction in which the oxidized graphite turns into the fully oxidized form CO_2 and the reduced graphene product. The released gas, mainly composed of CO_2 and H_2O, diffuses along the interlayer in an early stage of the decomposition, followed by an auto-accelerated reaction.[4] As a result of both processes, GO exfoliates. When GO is embedded in a polymer matrix, the chemical interactions at the GO surface might accelerate or slow down the GO reduction, as shown by the *in situ* reduction of GO in both poly(vinyl acetate) and poly(vinylpyrrolidone).[1] The reasons for these results are not clear, although based on previous studies by Dreyer et al.[5] on the reduction of GO by alcohols, Glover et al.[1] hypothesized that vinyl acetate groups in poly(vinyl acetate) are first hydrolyzed to alcohols and later oxidized to aldehydes by reacting with GO functional groups. In fact, GO is unstable not only to temperature but also to aging[6] as well as to the presence of water and organic solvents at room temperature.[7,8] Studies on the thermal decomposition of GO in our group have demonstrated that the presence of even trace amounts of organic solvents affects the mechanisms of thermal reduction: the higher the reducing power of the solvent (in terms of electron donation character), the lower the decomposition temperature of GO.[7,8]

In an intercalation compound, the polymer-host interactions are maximized, contrary to what happens in polymer-filler composites where polymer is the major phase and the presence of low amounts of fillers are almost "undetected" by the polymer chains far from the filler surface. This prompted us to study the thermal stability of polymers intercalated in GO. Our previous studies of PEO intercalated in GO (PEO/GO) demonstrated it to be a convenient platform for carrying out the

much-needed studies of macromolecular structure and dynamics under extreme two-dimensional (2D) confinement. PEO intercalates into the GO interlayer space, giving rise to a single molecular layer of thickness 3.0-3.4 Å.[9–11] Its concentration in the intercalate phase amounts to 22 $\pm$2 wt% of the total PEO/GO mass. Neither the interlayer spacing nor the amount of PEO depends strongly on polymer chain length, a strong indication that the oligomer and polymer chains are forced to adopt a planar conformation in a monolayer arrangement, i.e., well-defined and extreme 2D confinement. Moreover, PEO cannot crystallize in the intercalate, and its corresponding glass transition is not present in the calorimetric data.[9,10] Additionally, studying the vibrational properties of this system by using inelastic neutron spectroscopy,[9,10] we observed drastic changes in both the polymer conformation and the collective vibrational modes; these changes were a consequence of a predominantly planar zigzag (trans-trans-trans) chain conformation of the confined polymer phase. Surprisingly, these effects were largely insensitive to polymer chain length, suggesting the emergence of a new set of chain length scales primarily dictated by the presence of anchoring points on the GO substrate upon intercalation.[10]

In this work, we study the thermal stability of poly(ethylene oxide) (PEO) intercalated in GO (PEO/GO) by using thermogravimetric analysis (TGA) in isothermal and dynamic modes, TGA/mass spectrometry and temperature dependent X-ray diffraction. To investigate the effects of the reduction of GO on the stability of a PEO located outside of the interlayer, composite materials with 0.5, 5 and 50 wt% of GO in a PEO matrix were also prepared, and the results were contrasted with those of the PEO/GO intercalation compound. Moreover, isothermal TGA was run at various temperatures in the 150-180 °C range, allowing the establishment of the kinetic mechanisms involved in the thermal reduction of the PEO/GO intercalation compound. The results show that thermal degradation of the PEO/GO intercalation compound starts at 50 °C lower than pristine GO and 160 °C lower than neat PEO, due to a synergistic instability between GO and intercalated PEO. The kinetics show that the decomposition of the intercalation compound is largely dominated by the kinetic mechanisms of the GO reduction instead of being dominated by the polymer degradation. However, these kinetic mechanisms are modified by the presence of the polymer in

the interlayer, with the relative amounts of hydroxyl end groups and ethers in the intercalated PEO playing an important role. To complement our investigation of the thermal stability of PEO intercalated in GO, we also discuss the thermal stability of PEO adsorbed on graphene (G) and that of PVME, PAA, PVP and PAA adsorbed on the GO surface.

Experimental section

Graphite oxide was produced using natural graphite from Alfa Aesar (universal grade, 200-mesh, 99.9995% metal basis, reference number 40799). The starting graphite material was oxidized using a modified Brodie method.[4,12] In brief, the procedure was as follows. A reaction flask containing 200 mL fuming nitric acid (Fluka) was cooled to 0 °C for 20 min using a cryostat bath, followed by the immersion of 10 g of graphite. Next, 80 g of potassium chlorate (Fluka) was slowly added over a period of 1 h in order to avoid sudden increases in temperature. The reaction mixture was stirred for 21 h at 0°C. The mixture was then diluted in distilled water and filtered until the supernatant had a nitrate content below 1 mg/L (AQUANAL-plus nitrate (NO_3) 1-50 mg/L). The resulting GO slurry was dried at 80 °C for 24 h in a vacuum oven ($P < 0.1$ mbar) and stored in this oven at room temperature until further use. Elemental analysis of the GO obtained in this manner showed an atomic composition of stoichiometry $C_8H_{1.3}O_{2.7}$. Additional compositional information can be found in Ref.[13]

Graphene-like sheets (specimen G) were obtained by placing GO on a glass boat and inserting that into a quartz tube under an Argon flux. This tube was then loaded into a tube furnace preheated to 1000 °C. After 1 min, the tube was removed and cooled down to room temperature. Elemental analysis of the G so obtained showed an atomic composition of stoichiometry $C_8H_{0.1}O_{1.0}$.

Polymer uptake by the GO-based materials was performed in aqueous solution by stirring 0.5 g of polymer previously dissolved in 20 mL water with 0.5 g of GO and G for 15 days. (The resulting adducts are hereafter denoted as polymer/GO and polymer/G). Excess polymer was removed by filtration and thorough aqueous washings. The resulting polymer/GO and polymer/G were then

dried at 80 °C for 24 h in a vacuum oven (P < 0.1 mbar) connected to a dry scroll rotatory pump. All samples were kept dry in the vacuum oven at room temperature before testing.

PEO with increasing chain length [HO-$(CH_2CH_2O)_n$-H], where n=5, 13, 104, 795, and 2135, were used to prepare nPEO/GO intercalation compounds. (Note that we have used the term PEO indistinctly from poly(ethylene glycol) (PEG), because it is difficult to establish at which point PEG becomes PEO or vice versa). Composite materials were obtained by mixing PEO(n=2135)/GO intercalation compound with PEO(n=2135) in molten state, such that the final composition of the composites were 0.5, 5 and 50 wt% of GO. PEO(n=2135)/GO intercalation compound was used in all dynamic experiments and nPEO/GO (n=5, 13, 104, 795, and 2135) were used only for kinetic experiments in isothermal mode. A complete characterization of nPEO/GO intercalation compounds with different chain lengths is found in reference.[10] PEO(n=2135)/G was used for both dynamic and isothermal experiments. Structural characterization of PEO/G is found in references.[11,13] PVP (Mw = 1.6 x 10^5 g/mol), PAA (Mw = 1.8 x 10^3 g/mol), PVME (2.2 x 10^3 g/mol) and PVA (Mw = 1.1 x 10^5 g/mol) were also used for intercalation into GO as previously described.

Temperature-resolved XRD data in dynamic mode were collected upon heating at 1 °C/min from room temperature to 600 °C on a Bruker D8 Advance diffractometer operating at 30 kV and 20 mA, equipped with a Cu tube (λ = 1.5418 Å), a Vantec-1 PSD detector and an Anton Paar HTK2000 high-temperature furnace. Thermogravimetry in dynamic and isothermal modes was carried out in a TGA Q500 from TA Instruments, by using a constant N_2 flow of 60 mL/min. The same temperature programs as those in the XRD experiments were used. For the kinetic study of the nPEO/GO decomposition, isothermals were recorded at four temperatures in the 150-180 °C range; for the study of PEO/G and neat PEO they were recorded in the 290-330 °C range. The reliability of sample temperatures was carefully checked from the derivative thermogravimetric (DTG) peak corresponding to the Curie temperature of nickel.

TGA-MS was carried out using another TGA Q500, different from the previous one, coupled to a Pfeiffer Vacuum Thermo-StarTM mass spectrometer equipped with a channeltron detector. These dynamic experiments were recorded at 1 °C/min under constant He flow of 90 mL/min. The

evolved gas was ionized and its components detected according to the mass to charge (m/z) ratio.

Results and discussion

Dynamic experiments

PEO/GO intercalation compound

The graphic in Figure 1a gives a schematic representation of the intercalation of PEO into the GO interlayer on the basis of our previous experimental results.[9,10,13] Stated briefly, PEO intercalates into GO causing a significant expansion of the GO interlayer along the crystallographic c-axis, from 5.7 (bare GO) to 9.1 Å. The maximum uptake of PEO chains in the GO interlayer for a GO with an oxygen to carbon atomic ratio (O/C) of 0.34 is 22 $\pm$2 wt%,[13] a quantity that was determined to be largely independent of the polymer chain length.[10] On the contrary, the amount of intercalated PEO in GO was observed to increase from 9 to 27 wt% as the degree of oxidation (in terms of O/C) goes from 0.29 to 0.38.[13]

One of the main characteristics of these PEO/GO intercalation compounds is their early decomposition, at 50 °C lower than that of pristine GO, and at 160 °C lower than neat PEO, as observed in the thermogravimetric analysis (TGA) presented in Figure 1b. This behavior, we found, is independent of the chain length of PEO and of the degree of GO oxidation. As illustrated in the figure, the weight loss and first derivative of the thermogravimetric data (DTG) for PEO/GO show that the thermal decomposition of this compound occurs in two main steps, at 195 and 287 °C, whereas that for pristine GO and neat PEO occurs at 243 °C and 355 °C. These values correspond to the temperature at the peak maximum (Tp) of the DTG.

To analyze the origin of the weight loss at 195 and 287 °C in PEO/GO, TGA-MS measurements of PEO/GO were performed at a heating rate of 1 °C/min in helium (Figure 2). These data are compared to that of pristine GO reported in a previous study in our group[4] and that of neat PEO (Figure 2). Note that TGA data obtained in the TGA-MS experiment do not match exactly those

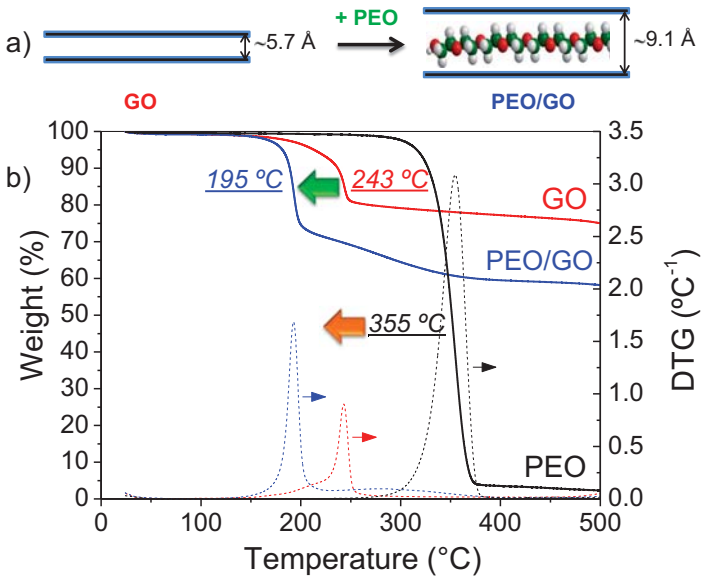

Figure 1: a) Sketch of PEO intercalation into GO interlayer causing an expansion from ca. 5.7 to 9.1 Å. b) TGA and DTG showing the decrease in decomposition temperature of pristine GO and neat PEO when PEO is intercalated into GO interlayer (PEO/GO). The composition is 24 wt% of PEO in PEO/GO, which corresponds to the maximum uptake of PEO in GO. Tp of PEO/GO is 50°C lower than that of pristine GO and 160 °C lower than neat PEO. Heating rate: 1°C/min, atmosphere: nitrogen.

shown in Figure 1b, because the thermal stability of PEO/GO in helium is ∼15 °C higher than that in nitrogen (see Supporting Information).

Neat PEO decomposes in one step at Tp = 360 °C in helium. The evolved gas in the neat PEO revealed the existence of a wide range of ion fragments: m/z ion peaks appear at 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60. The degradation mechanism of PEO is known to proceed via random-chain scission of C-O bonds and C-C bond cleavage,[14–16] leading to the formation of a series of molecules such as mono and diether oligomers, ethylene glycol, diethylene glycol, 1,3 dioxolane, 2-methoxy-1,3 dioxolane, methyl vinyl ether, ethyl vinyl ether, 2-butenal,[17,18] and also furan, oxalic acid, ethylene oxide, and oxymethylene species.[14] The fragment ions observed in the MS profiles would correspond to these species and to their fragmented products.

The presence of PEO in PEO/GO was identified by the characteristic m/z signals of PEO pre-

viously described. The following m/z signals were found in PEO/GO (Figure 2): 12, 13, 15, 17, 18, 20, 22, 24, 25, 26, 29, 30, 31, 41, 42, 43, 44, 45, 46, 50, 56, 57, 58, 60. Signals with m/z = 12, 18, 43, 44, 45, 46 and 50 are common to both GO and PEO/GO. Ion signals with m/z = 18 have been ascribed to H_2O (H_2O^+) and those with m/z = 12, 44, 45 and 46 to CO_2 [12 (C^+), 44 (CO_2^+), 45 ($13CO_2^+$), 46 ($C^{18}O^{16}O^+$)].[4] The low intensity signal with m/z = 43 could arise from $C_2H_3O^+$ fragments. The remaining signals with m/z = 13, 15, 17, 20, 22, 24, 25, 26, 29, 30, 31, 41, 42, 56, 57, 58, 60 in PEO/GO are characteristic of PEO decomposition. Therefore, the presence of all these ions in the first weight loss occurring at 213 °C and ions with m/z = 26, 57 and 58 appearing in the second weight loss at 305 °C implies that PEO in PEO/GO decomposes in two stages, both of them at lower temperatures than neat PEO.

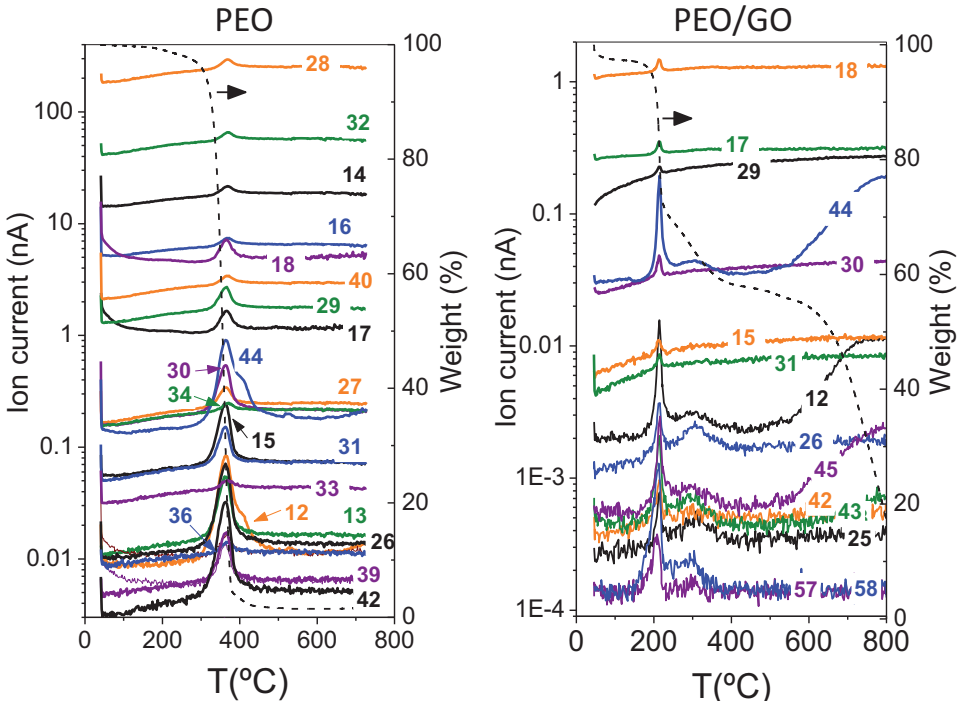

Figure 2: TGA-MS of neat PEO and PEO/GO obtained at a heating rate of 1 °C/min in helium. Left axis: ion current for fragments with m/z as indicated in the MS lines. Right axis: weight loss. Additional signals for neat PEO with ion currents lower than 0.003 nA are shown in the Supporting Information.

To identify the temperature at which the thermal reduction/exfoliation of GO in PEO/GO occurs, temperature-resolved XRD of PEO/GO was obtained by using a dynamic heating program up

to 600 °C (Figure 3). At temperatures lower than about 200 °C, PEO/GO displays XRD patterns with two well-defined (001) and (002) reflections. With increasing temperature, both reflections show an important intensity loss until their total disappearance and the concomitant emergence of a new peak at 2θ = 22-26°. This new signal has been ascribed to the 002 reflection of graphite-like structures as a result of the partial restacking of reduced GO layers.[4]

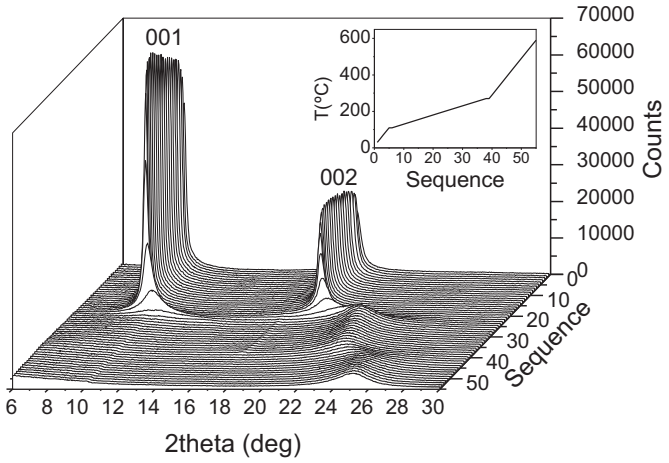

Figure 3: Temperature-resolved XRD profiles for PEO/GO. Inset: Correspondence of temperature with sequence of the 3D graph.

Figure 4 shows the variation of the interlayer distance, calculated from the Bragg diffraction angle of the 001 peak, and the variation of the integrated peak areas as a function of the temperature. These data are compared with that of the weight loss obtained by TGA. From room temperature to 185 °C, the loss of 1 wt% absorbed moisture occurred, but with insignificant changes in the interlayer distance (special care was taken by rapidly moving the sample from the vacuum oven to the TGA equipment). However, this small water loss affected the 001 peak area, which showed a marked increase. Because the peak area intensities are a true measure of the amount of stacking layer present, the results suggest that water deintercalation allows the GO layers to stack in a more ordered fashion. This behavior was also found in temperature- and time-resolved XRD studies on water desorption from GO.[4,12,19]

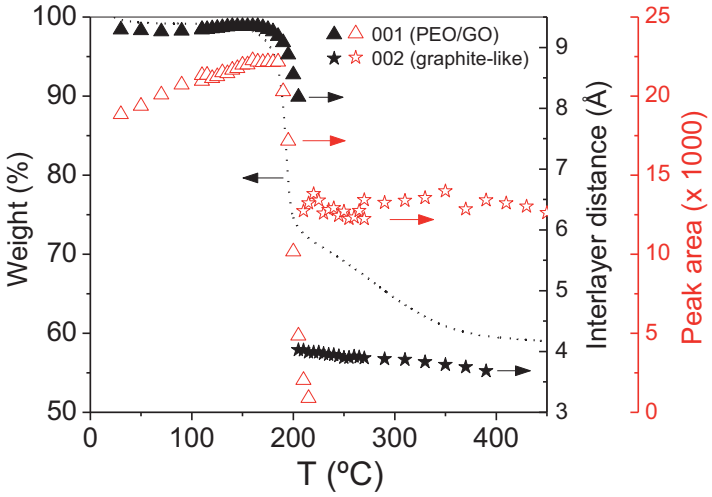

Figure 4: Overlapping of TGA profile with the variation of the interlayer distance obtained from the 001 reflexion of PEO/GO and that of the 002 reflexion of the graphite-like structure in the temperature-dependent diffractograms. Data of peak area of the 001 reflexions of PEO/GO and those of 002 reflexions of the graphite-like structure are plotted in the red right axis.

At temperatures higher than 185 °C, the 001 peak area showed a dramatic reduction down to the detection limit with a concomitant collapse of the interlayer distance of GO layers. The close overlapping of both mass loss and 001 peak area decrease indicates that decomposition leads to a complete loss of any stacked-layer structure in PEO/GO. Most of the GO layers exfoliate (decreasing peak area), while others seem to move closer together (decreasing interlayer distance) due to the release of the gas produced upon the decomposition of both GO and PEO out of the interlayer. At the end of this process, the 001 and 002 peaks of PEO/GO disappeared and the 002 reflection from graphite-like structures emerged. The interlayer distance of the latter structures continued decreasing (from 4.0 to 3.6 Å) with the temperature while the peak area was almost constant. This process was accompanied by about 10 wt% weight loss.

The results of dynamic TGA, TGA-MS and temperature-resolved XRD provided us with an important set of data on the thermal decomposition of PEO/GO, namely: 1) the decomposition of PEO in PEO/GO starts at 185 °C in nitrogen, ca. 160 °C lower than that of neat PEO, and is extended over a broad temperature range (from 185 to 400 °C); 2) PEO in PEO/GO decomposes in two main steps, the first at Tp = 195 °C and the second at 287 °C; 3) the thermal reduction of

GO starts at 185 °C, ca. 50 °C lower than that of pristine GO, causing the complete loss of the stacked-layer structure in PEO/GO. These results suggest that either the thermal reduction of GO initiates the decomposition of the PEO chains intercalated in the GO interlayer, or PEO promotes the degradation of GO. In addition, the fact that PEO chains in PEO/GO are under considerable internal strain as a result of their extended planar zig-zag conformation, distinct from that in the bulk,[9,10] and that they are strongly interacting with GO sheets, it is expected that the increase of the molecular motion upon heating facilitates the rupture of the polymer backbone more than in the bulk polymer,[20] where the chains are free to slide one along another. However, ascribing the origin of the thermal instability to PEO or GO in the intercalate is not straightforward. The results seem to indicate that upon being heated, both PEO and GO destabilize each other synergically.

Composites of PEO and GO

To detect possible effects of the reduction of GO on the stability of a PEO located outside of the interlayer, composite materials with 0.5, 5 and 50 wt% of GO in a PEO matrix were prepared. These samples were obtained by mixing proportional parts of the intercalation compound PEO/GO (PEO:GO mass ratio = 24:76) and PEO in molten state. Figure 5 (a and b) shows the TGA and DTG of the obtained samples. These data were compared with that of neat PEO. The TGA profiles show that the step at ca. 200 °C decreases with the increase of the polymer amount in the composite, while that occurring at ca. 355 °C increases, as expected. Therefore, the presence of these two clear regions in the thermograms shows the following: the region at ca. 200 °C is connected with the thermal reduction of GO, while the region at 355 °C is linked to the decomposition of PEO outside of the interlayer.

The Tp values of the above-mentioned processes obtained from the DTG profiles are displayed in Figure 5b. The data show that the Tp of the process at a lower temperature is similar for all composites but that of the process at a higher temperature increases from 343 to 353 °C in going from a composite with 50 to 0.5 wt% of GO. Moreover, the Tp values of the composites with 5 and 0.5 wt% of GO are the same than that of neat PEO. These results indicate that whereas

the thermal stability of GO in intercalation compounds is not affected by the massive presence of PEO outside of the interlayer, that of the bulk PEO is reduced by up to ten degrees by the presence of 50 wt% of GO in the composite. However, for composites with a lower amount of GO, the stability of the polymer is not substantially affected. The opposite behavior was found for intercalation compounds of PEO in montmorillonite, where intercalated PEO showed higher thermal stability than that outside the galleries in an oxygen atmosphere.[21] This was attributed to a slower diffusion of oxygen and the degradation products inside the interlayer, as well as to the fact that montmorillonite is thermally stable in the temperature range where PEO decomposes.

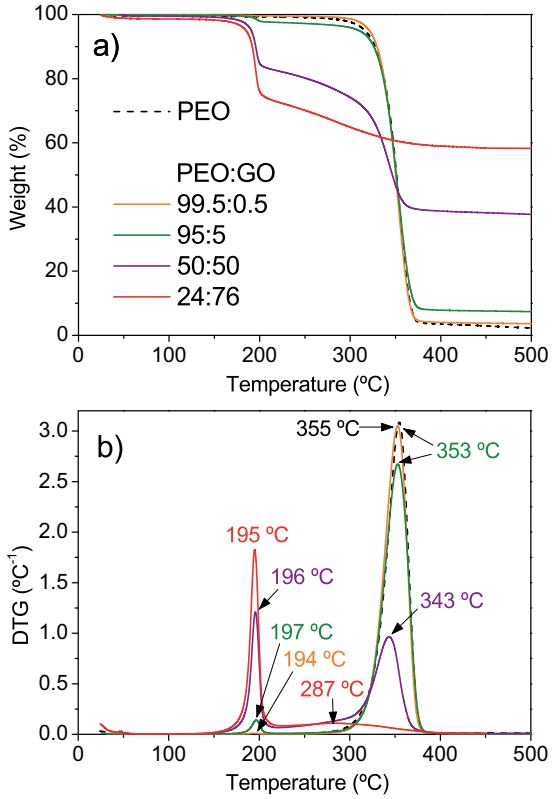

Figure 5: a) TGA and b) DTG data of composites of PEO and GO with GO contents of 0.5, 5 and 50 wt%. The data are compared with that of the intercalation compound (76 wt% GO) and neat PEO. Heating rate: 1°C/min, atmosphere: nitrogen.

The weight loss already detected for the intercalation compound (76 wt% of GO) at Tp = 287 °C was also observed for the composite with 50 wt% of GO but was not detected in the rest

of the composites. As described above in the discussion of temperature-resolved XRD, at this temperature the reduced GO layers are mostly exfoliated and some of them are stacked to form graphite-like structures. Therefore, the process occurring at Tp = 287 °C could be related to the decomposition of PEO near the reduced GO surface. With decreasing GO content in the composite, the amounts of PEO near the surface are lower, and therefore this event is more difficult to detect.

The results shown so far suggest that the thermal decomposition of the GO-PEO composites starts in the interlayer of GO by a combination of events where the GO and the intercalated polymer decompose. In this process a mixture of volatiles and solid residues are produced, fueling the decomposition of the polymer near the reduced GO surface. On the other hand, the presence of this surface acts as a barrier to the diffusion of the volatiles, preventing further reactions with the polymer far from the surface. As a result, the lower the amount of GO in the composite, the smaller the effects of this filler on the thermal stability of the bulk polymer.

Isothermal Experiments

Kinetics of the thermal decomposition of PEO/GO intercalation compounds

To determine the kinetic mechanism of the thermal decomposition of the PEO/GO intercalation compound, isothermal TGA was recorded at different temperatures (see Supporting Information). Figure 6 shows the rate of weight loss (dW/dt) as a function of percentage weight loss (W) at 160 °C for a series of PEO/GO with increasing chain length (n) of PEO, where n is defined as the repetitive ethylene oxide units in PEO [$HO(CH_2CH_2O)_nH$]. For comparison, the data for pristine GO at 190 °C is also included. Note that pristine GO is thermally more stable than PEO/GO; therefore, we cannot compare the isothermal data at the same temperature.

In a previous study we determined that the isothermal reduction of our Brodie-based GO followed two distinct kinetic mechanisms associated with either diffusion or autocatalytic decomposition, as depicted in Figure 6.[4] The first mechanism manifested itself at the beginning of the thermal reduction of GO through a rapid decrease of the rate as a function of the weight loss. The second mechanism followed the first one and showed a maximum rate. In the case of the intercalation

compounds, the first mechanism was barely detected with increasing chain length, with the second mechanism being predominant over the whole weight loss process.

The rate of reaction is described by the general equation $d\alpha/(dt)=k(T)f(\alpha)$, where α is the degree of conversion, k(T) is the temperature-dependent rate constant and $f(\alpha)$ depends on the reaction mechanism. The isothermal curves for PEO/GO were fitted to a mathematical expression of an autocatalytic reaction:[22] $f(\alpha)=\alpha^M(1-\alpha)^N$, where M and N have only an empirical significance. These values determine the relative contributions from the acceleratory and decay regions. For the fitting, M was successfully fixed to 4 while N parameter was varied independently (results are shown in Table 1). In the case of PEO/GO with n=5, a distinct mechanism from that of autocatalysis was distinguished at the beginning of the decomposition, yielding a weight loss of only about 2 wt% at 160 °C. The rate of weight loss in this part of the curve seems to follow a 2D-diffusion like that found in pristine GO. However, as there are insufficient data points in this range of weight loss and as this process can no longer be detected when the temperature is increased, it was not possible to fit it to some mathematical function $f(\alpha)$. On the other hand, the parameter k(T) obtained from the fitting with the autocatalytic model followed the Arrhenius equation, from which the activation energy (Ea) was obtained. Table 1 shows the parameters M, N and Ea determined for the isothermal decomposition of PEO/GO as a function of the chain length of PEO (n). These values are compared with those obtained for a pristine GO in our previous study.[4] The most significant characteristics of these kinetic parameters are the variation of the N parameter from 4 to 2 in going from shorter (n=5 and 13) to longer chain lengths, and the fact that Ea is slightly lower for the PEO/GO compounds than for GO.

To interpret these results, we need to consider the interactions between PEO and GO. PEO forms hydrogen bonds between PEO ether groups and GO hydroxyls as well as between PEO hydroxyl end-groups and GO epoxy groups, as observed through infrared spectroscopy in our previous studies.[10] The molar ratio of PEO oxygen to OH groups in GO and that of PEO hydroxyls to epoxy groups in GO as a function of the chain length of PEO are shown in Figure 7. As expected, the molar ratio of PEO oxygen to OH groups in GO increases with the chain length, whereas the

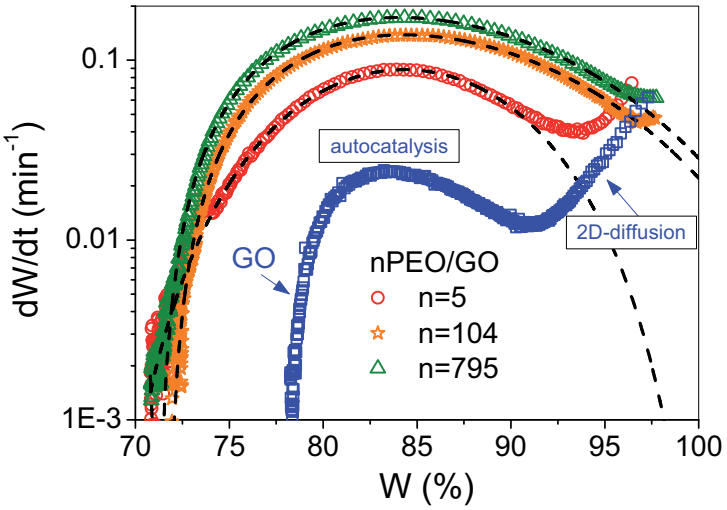

Figure 6: Rate of weight loss (dW/dt) of PEO/GO as a function of percentage weight loss (W) at 160 °C in nitrogen atmosphere. Intercalation compounds with PEO of increasing chain length (n) are compared. Data for pristine GO is also showed (T = 190 °C). Dashed lines depict the fitting curves obtained with an autocatalytic model.

Table 1: M and N parameters obtained from the fitting of the isothermal curves by using a mathematical function for an autocatalytic reaction. Ea of the autocatalytic mechanism in the thermal decomposition of GO and nPEO/GO, where n denotes the PEO chain length.

nPEO/GO	M	N	Ea (kcal/mol)
GO	4	1.5	38
5PEO/GO	4	4	35
13PEO/GO	4	4	33
104PEO/GO	4	2	34
795PEO/GO	4	2	31
2135PEO/GO	4	2	32

ratio of PEO hydroxyls to epoxy groups in GO decreases. The maximum ratio reached in our PEO/GO systems is 0.8. This value implies that the maximum probability to find an interaction via hydrogen bonds between intercalate and host is 0.8, a value which is very high, close to the maximum value found (1.0) for these type of PEO/GO systems.[13] With this picture in mind, the decreasing N parameter with the increasing chain length obtained in the kinetic experiments could be linked to the effects of the end groups of PEO on the mechanisms of thermal decomposition of PEO/GO. As a low value for N implies a higher rate in the decay region of the decomposition curve, the kinetic results seem to indicate that the lower the amount of OH end groups in PEO (longest

chains), the higher the decomposition rate at the latest stage of the transformation. Therefore, when the interactions of PEO ether groups and GO hydroxyls are maximized, the decomposition is accelerated at the ultimate stage and becomes similar to that in pristine GO. Nevertheless, the effects of the polymer end groups on the activation energy are not evident. On the other hand, the fact that we can not detect the diffusion mechanism in PEO/GO with longer chain lengths would indicate that the GO interlayer space is highly occupied, impeding the release of the gas produced upon heating.

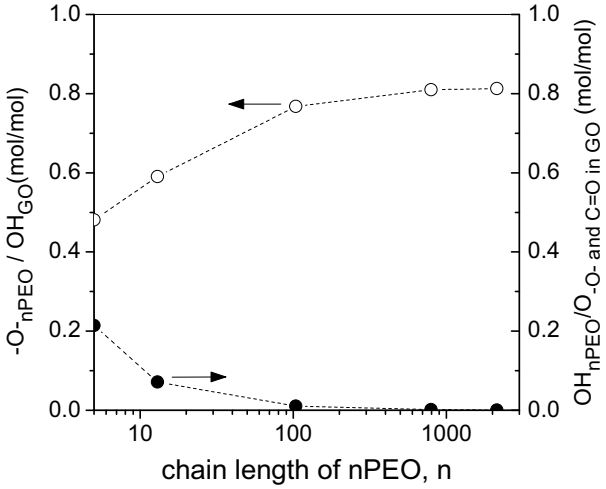

Figure 7: Molar ratio of PEO oxygen to OH groups in GO (left axis) and that of PEO hydroxyls to epoxy groups in GO as a function of the chain length (n) of PEO.

Since the decomposition of PEO/GO at about 200 °C involves both processes—the decomposition of PEO and the reduction/expansion of GO—it is not possible to unequivocally ascribe the overall kinetic mechanism to the decomposition of PEO or GO, although the similarities of the kinetic formalism to that of pristine GO suggest that the parameters obtained in Table 1 would correspond to the thermal decomposition of GO in the intercalation compound. One way to approach the study of the kinetic mechanisms of PEO adsorbed on GO is to monitor the degradation of PEO adsorbed on thermally reduced/exfoliated GO, also called graphene.

Kinetics of the thermal decomposition of PEO adsorbed on graphene

Graphene (G) was observed to take up to 28 wt% of PEO.[11] Moreover, given the exfoliated nature of G layers, PEO can accommodate itself onto the G surface by adopting relatively free molecular conformations—unlike the PEO chains intercalated in GO layers, where geometrical constraints dictate the monolayer arrangement of the polymer phase. The thermal stability of the adsorbed PEO is dictated by its interactions with the G substrate, where it is likely that the remanent hydroxyl groups in G form hydrogen bonds with PEO ethers. The PEO-oxygen-to-substrate OH ratio in PEO/G is 8.9, implying that there are about 9 monomeric PEO units per G OH.[11,13] DTG data of PEO/G, shown in Figure 8a, show that, contrary to the PEO/GO intercalation compound, the thermal stability of PEO is close to that of bulk PEO. In this case, PEO shows its major decomposition at 365 °C (26 wt% loss), which is ca. 20 °C lower than neat PEO. Small peaks observed at a lower temperature are associated with 1 (226 °C) and 2 wt% loss (265 °C); their origins are not clear.

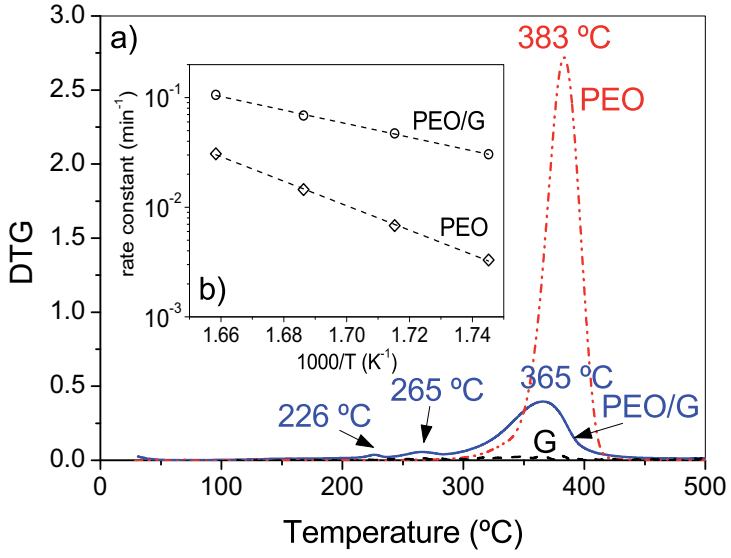

Figure 8: a) DTG data of PEO/G, neat PEO and G. Heating rate: 10°C/min, atmosphere: nitrogen. b) Arrhenius plot of the decomposition rates for neat PEO and PEO/G.

Isothermal TGA data for PEO/G and neat PEO were fitted to a first-order reaction function, $f(\alpha)=(1-\alpha)^n$, n = 1. The temperature dependence of the rate constants obtained from the fitting

follows the Arrhenius equation (Figure 8b), in which it is apparent that the Ea for the thermal degradation of PEO adsorbed on G (28 kcal/mol) is considerably lower than that for neat PEO (48 kcal/mol). The latter value is in agreement with that found for high molecular weight PEO (30-50 kcal/mol) in existing publications.[15,23] However, the clear differences in the Ea for PEO/G and neat PEO in the present study suggest that polymer-graphene interactions favor the cleavage of polymer bonds in pyrolysis conditions. It is known that simple adsorption of brush-like polymers with long side chains on a substrate can induce spontaneous rupture of covalent bonds in the macromolecular backbone.[20] This is not exactly our case, as PEO has a linear structure and degradation occurs at high temperatures, but it is likely that adsorption induces tension along the polymer backbone and that these forces increase with the molecular motion resulting from heating.

Hydrophilic polymers with side groups

In order to study the effects of functional groups on the thermal degradation of polymer/GO, compounds of GO and PVME, PVA, PAA and PVP were obtained by using the same procedure as that for the PEO/GO intercalation compound. One common characteristic of these polymers is that they contain side hydrophilic functional groups. These side groups interact with GO by hydrogen bonds, allowing the intercalation and retention of large amounts of polymer as reported in Table 2. We also observed that the presence of these side groups notably affected the GO stacking by producing either exfoliation or partial intercalation. The XRD data presented in Figure 9 shows that the intensity of the 001 peak of GO decreases upon intercalation, and that the polymer/GO compounds lack intense diffraction features as compared to the PEO/GO intercalation compound. In the case of PVME/GO and PVP/GO the presence of a small feature at 1.1 ($Å^{-1}$) (close to that of GO) indicates that there exist regions in the sample where the polymer cannot intercalate and, therefore, the regions remain empty. In all cases we observed small features at lower Q, suggesting intercalation but lacking a defined structural order. Given these premises, we can not say that the polymer is in an intercalation regime, but it is adsorbed on exfoliated GO sheets. We should note that these polymer/GO compounds are free of metals like Na^{+} and Cu^{2+}, which have been used

to prepare intercalation compounds of PEO,[24–26] PVP[26] and PVA,[25] and GO. In those systems, well-defined stacking structures were observed for PVP/GO and PVA/GO with interlayer spacings of 16.7 $Å^{-1}$ and 13.2-22.1 $Å^{-1}$, respectively. However, none of these works clarify the effects of the metal cation on the intercalation process. It is very likely that the overall structure of GO is strongly dependent on the presence of these species as, for example, sodium hydroxide can be used quite effectively to reduce the oxygen content of GO.[27] In our case, XRD results suggest that the arrangement of polymers containing side groups in the GO interlayer is completely different from that of PEO, which is known to adopt a planar zig-zag conformation.[9–11]

Table 2: Amounts of polymer taken up by GO. Decomposition temperatures at Tp found for the polymer/GO compounds and their corresponding bulk polymers. Last two columns show the temperature variation respect to pristine GO and neat polymer. Heating rate: 1°C/min, atmosphere: nitrogen.

polymer/GO	uptake (wt%)	$Tp_{polymer}$ (°C)	$Tp_{polymer/GO}$ (°C)	$Tp_{polymer/GO}$-Tp_{GO} (°C)	$Tp_{polymer/GO}$-$Tp_{polymer}$ (°C)
PVA/GO	40	215, 380	180, 216, 313, 388	-63	-35
PVP/GO	25	389	201, 373	-42	-188
PEO/GO	24	355	195, 287	-48	-160
PAA/GO	17	220, 294, 395	207	-36	-13
PVME/GO	14	374	184, 225, 308	-59	-190

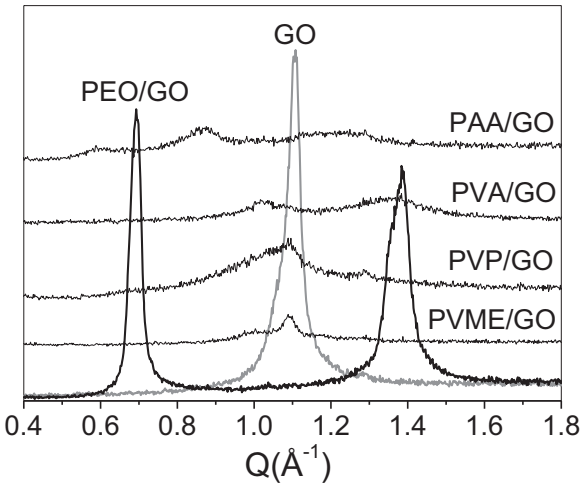

Figure 9: XRD of compounds of GO and PVME, PVA, PAA and PVP. XRD data of the PEO/GO intercalation compound and pristine GO are also shown.

Despite the lack of a defined structural order for our PVME/GO, PVA/GO, PAA/GO and

PVP/GO, the TGA and DTG data of these series of compounds shown in Figure 10 and the Tp values in Table 2 indicate that all the polymer/GO compounds start decomposing at lower temperatures than either pristine GO or their own corresponding bulk polymers. These results indicate that interactions at the GO surface play an important role in the thermal stability of both polymer and GO. The highest Tp reduction with respect to that of pristine GO was observed for PVME/GO and PVA/GO, a result that might suggest that the most destabilizing polymer-GO interactions for GO are those comprising ether and alcohol groups in the guest material. From the point of view of the polymer, the highest reduction in decomposition temperature was observed for PVP, PEO and PVME, which showed up to 190 °C of difference respect to neat polymer. This result confirms that the presence of GO notably reduces the thermal stability of these functional polymers.

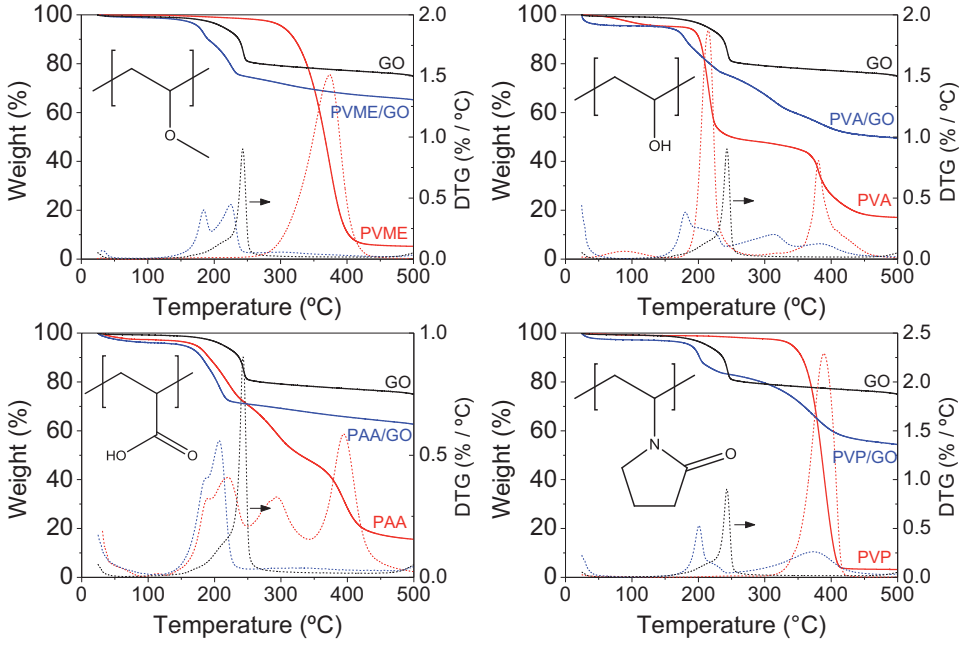

Figure 10: TGA and DTG for compounds of GO and PVME, PVA, PAA and PVP. TGA data of bulk polymers and pristine GO are also shown. Heating rate: 1°C/min, atmosphere: nitrogen.

Analysis of the multiple weight loss events occurring in both the bulk polymers and the polymer/GO is not straightforward. However, we can observe that in the case where the bulk polymer has a single weight loss such as in PVME and PVP, we can clearly distinguish a weight loss at

a temperature close to that in the bulk polymer, albeit at a significantly lower temperature (see Table 2). This weight loss corresponds to the degradation of the polymer close to the surface, as found in the composites of PEO and GO.

Conclusions

In this study we have demonstrated that the presence of an adsorbing surface, whether thermally unstable like GO or thermally stable like graphene, reduces the thermal stability of the polymer close to and directly adsorbed on the surface. In addition, the thermal stability of GO is also significantly reduced by about 50 °C due to interaction with the polymer. These conclusions are supported by the dynamic TGA studies of a series of compounds, where different hydrophilic polymers were intercalated into GO, leading to well-defined stacked structures (such as in the PEO/GO intercalation compound) and polymer-adsorbed GO structures (such as in the PVME/GO, PVA/GO, PVP/GO and PAA/GO compounds). In composites, where the polymer is both inside and outside the interlayer, a different picture emerges. In this case, we detect three decomposition steps, one associated with the synergistic decomposition of PEO and GO at lower temperatures, the second one related to the degradation of the polymer adsorbed on the reduced and expanded GO surface and the third one involved in the decomposition of the polymer chains far from the surface.

The kinetics study of the thermal decomposition of the PEO/GO intercalation compound showed that an an autocatalytic mechanism similar to that found for pristine GO in a previous study of ours dominates the overall process.[4] However, the kinetic function used to fit the rate curves showed a dependence on the chain length of PEO, suggesting that the reaction kinetics are affected by the relative amounts of hydroxyl end groups and ethers in the intercalated PEO. On the other hand, the kinetics of the thermal degradation of PEO directly adsorbed on graphene demonstrate that interactions with this adsorbing substrate reduce significantly the activation energy of the polymer decomposition by 20 kcal/mol as compared to neat PEO.

These findings underline the importance of considering substrate-polymer interactions in the

thermal stability of polymers for an appropriate design of composite materials.

Acknowledgements

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Supporting Information

Complementary TGA-MS data of neat PEO; comparison of TGA data of PEO/GO in nitrogen and helium; and isothermal TGA of 2135PEO/GO. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Thermal stability of polymers confined in graphite oxide

Fabienne Barroso-Bujans, Angel Alegría, Jose A. Pomposo, and Juan Colmenero